

# EFFECTS OF COPPER ORE ON THE ECOLOGY OF A LAGOON

By Kenneth T. Marvin and Larence M. Lansford, *Chemists*, and Ray S. Wheeler, *Fishery Research Biologist*,  
Bureau of Commercial Fisheries

Sudden, immense increase in the plankton population has resulted in extensive destruction of commercially important fish and shellfish. Sometimes this fish-killing plague is known as "red tide" because of the amber to dull-red discoloration of the water.

The organism present in frequent occurrences of red tide in Offats Bayou, Galveston (Tex.) was identified by Gunter (1942), and by Gates and Wilson (1960), as *Gonyaulax monilata*. *Gymnodinium breve* was identified by Davis (1948) as the cause of destructive red tide blooms that have occurred off the west coast of Florida at irregular intervals since, at least, 1844 (Feinstein and others, 1955).

Following the outbreak of destructive *G. breve* blooms in 1946 and 1947, the U.S. Bureau of Commercial Fisheries began a study of the organism and the environmental factors limiting or promoting its growth, to develop, if possible, a means of controlling or, at least, reducing the occurrence of these lethal outbreaks.

The toxic property of copper has been employed elsewhere with varying degrees of success in related occurrences of plankton blooms. Experiments in the U.S. Fish and Wildlife Service Laboratory have demonstrated that the minimum amount of dissolved copper lethal to *G. breve* is about 0.5 microgram atoms per liter (0.03 p.p.m.). An experiment was designed therefore to test the feasibility of using immersed copper ore as a source of copper in lethal concentrations through its release into solutions over a rather long period of time.

We wish to express our appreciation to Mrs. Zoula Zein-Eldin, William Wilson, and Drs. David Aldrich and Abraham Fleminger, who conducted many of the analyses, and to the Morenci Mining Branch of the Phelps Dodge Copper Corporation for furnishing the copper ore for the experiment.

## COPPER ORE EXPERIMENT

The experiment was designed to determine whether or not immersed ore would affect the flora and fauna. This would be decided by comparing chemical and biological studies made before and after the addition of ore.

Questions to be resolved were the following:

(1) Could copper concentration in a body of water be raised to a level lethal to *G. breve* by the permanent exposure of a reasonable amount of copper ore? (2) Would the copper concentration of the water remain at a constant level? (3) Would the copper have an adverse effect on other marine organisms?

To obtain an estimate of the amount of copper ore needed, laboratory studies were made on the solubility of the copper in various amounts of ore in tanks of sea water. On the basis of the results of these tests, 20 tons of ore seemed a reasonable amount with which to start. Subsequent dosages, if necessary, would be based on the results of the first addition. We used a sulphide ore that contained approximately 1 percent copper and 3.5 percent iron. The particle size varied from dust to coarse gravel.

The questions were answered (1) by observing the effects of the ore on two indicator organisms,<sup>1</sup> (2) by determining the level of the copper concentration maintained, and (3) by comparing ecological conditions of the lagoon before and after the addition of the ore. Comparisons were based on gross differences in productivity of the water, on significant changes in mortality rates of organisms, and on variation in barnacle setting rate. Chlorophyll and zooplankton analyses were used as indicators of productivity. Mortality rate

<sup>1</sup> Laboratory experiments demonstrated that the tolerance of these organisms to copper was approximately the same as that of *Gymnodinium breve*. One of these, *Prorocentrum* sp., was placed in the lagoon in dialysis bags, another, *Gymnodinium splendens*, occurred naturally in the lagoon.

NOTE.—Approved for publication September 12, 1960. Fishery Bulletin 184.

studies were made of *Gymnodinium splendens* that occurred in the water, and of organisms from the live cars: oysters, *Crassostrea virginica*; mullet, *Mugil cephalus*; and two snails, *Littorina irrorata* and *Thais* species.

Our field activities were conducted in a man-made lagoon located on the eastern end of Galveston Island (fig. 1). The lagoon, 1.1 statute miles long, has an estimated volume of about 230 acre-feet and is connected to the Galveston Ship Channel by seven 36-inch cement culverts. Chemical and biological samples were taken at eight stations. Samples were collected three to four times a week until the first ore addition of 20 tons was made and then twice a week. Several months after the final addition of 40 tons, the rate was reduced to once a week and the number of stations sampled to three (stations 1, 4, and 7). During collection trips samples were taken for salinity, copper, chlorophyll, *G. splendens*, and zooplankton analyses. The water for these was taken with a stainless steel neoprene impeller pump. During collections the intake end of the polyethylene connection hose was continuously raised and lowered from a few inches of the bottom to the surface. Thus, the samples were represent-

ative of the entire column. A 4-inch Secchi disc reading was also taken at each station. Once or twice a week, depending on weather conditions, a count was made of the organisms in the live cars anchored at each station. At weekly intervals, barnacle-setting plates were suspended 2 feet below the surface at each station. These plates were replaced every week.

Before each addition of ore, dialysis bags containing cultures of known concentrations of *Prorocentrum* sp. were suspended in perforated polyethylene bottles 2 feet below the surface at stations 2, 4, 5, 6, and 7. These bottles were replaced so that some of them remained in the water for 2 days and others for 4 days. The first of these experiments was discontinued 2 weeks after the first ore addition and the second, 1 week after the second addition.

## ANALYTICAL METHODS

### Chlorophyll

The chlorophyll analyses consisted of estimations of chlorophyll a, b, and c in acetone extracts of plant and animal material. The method employed was that of Richards with Thompson (1952) as modified by Creitz and Richards (1955).

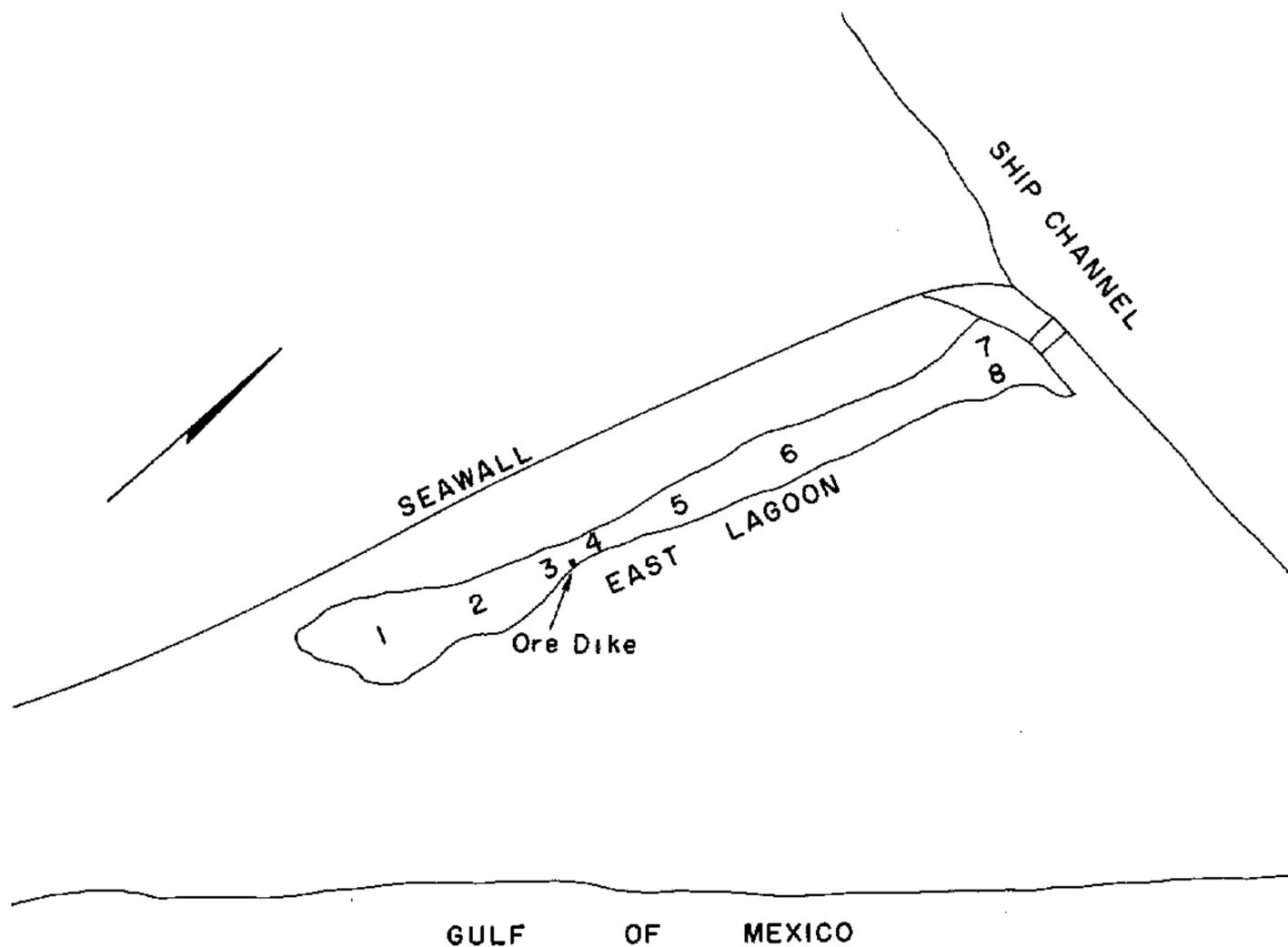


FIGURE 1.—East Lagoon station locations selected for the copper ore experiment.

### Salinity

Salinity values were estimated from density-temperature measurements taken with a hydrometer calibrated to the nearest 0.2 of a salinity unit (‰) and a centigrade thermometer calibrated to the nearest unit.

### *Gymnodinium splendens*

Two-liter water samples for *G. splendens* analyses were placed under fluorescent lights for about 16 hours. This concentrated the organisms in the upper part of the container. A preliminary examination was made of a portion of the sample taken from the meniscus. If *G. splendens* were not observed, a zero count was assumed for the sample. If in evidence, the top 200 ml., which contained virtually all of the *G. splendens*, were carefully siphoned into a flask and thoroughly mixed. Ten 1-milliliter samples were removed and counted for *G. splendens*. The average of these was converted to count per liter by multiplying by 100. An alternative method used for high-count samples was similar except that the 10 portions were taken from the entire mixed sample. The conversion to count-per-liter was obtained by multiplying the average by 1,000.

### Copper

To determine the copper concentration, we used the method described by Hoste, Eeckhout, and Gillis (1953). This was preferred to that of Chow and Thompson (1952) because the latter method is not so selective for waters of variable pH, such as is found in the lagoon. Further, when coastal and bay waters are analyzed by this method, a turbid extract forms occasionally that is difficult to analyze.

### Zooplankton

The zooplankton samples were obtained by pumping 250 gallons of water through a plankton net of No. 2 bolting silk. These were diluted to 100 ml., and an aliquot part checked for the various types of zooplankton. The count of each was recorded as count per 100 liters by multiplying by the appropriate factors. The size of the aliquot part varied, depending on the population density of the sample.

### Barnacle setting rate

The barnacle attachment rate was based on the average daily setting-rate on 4-inch square cement

plates suspended horizontally 2 feet below the surface at each station. The rate was estimated by averaging the count per square centimeter of eight locations on each plate, and then dividing by the number of days that the plate was submerged in the lagoon.

### *Prorocentrum* sp.

We used Wilson's (1959) dialysis membrane bag method for evaluating the effects of the copper ore on *Prorocentrum* sp. cultures suspended in the lagoon. Initial and final population estimates were made by counting the organisms in several 0.01 ml. portions taken immediately before the culture was placed in the dialysis bags and after their removal from the lagoon.

## RESULTS

### Chlorophyll

The results of the chlorophyll a, b, and c analyses are shown in figure 2. We have placed the November 1958 to April 1959 section of the graph under the corresponding months of 1957 and 1958 to simplify seasonal comparison. The phytoplankton blooms noted during November 1957 and January to March 1959 were reduced during the corresponding months of 1958 and 1959. Whether or not this was an effect of the ore is not known. The significant fact shown is the continued productivity of the lagoon after the addition of ore. This is indicated by the continuation of chlorophyll concentrations that are representative of a highly productive area (Zein-Eldin, 1959).

### Salinity

Figure 3 shows monthly salinity ranges and averages of the lagoon. All data are based on the average of station salinity values.

### *Gymnodinium splendens*

The average population of *G. splendens* in the lagoon from November 1957 to June 1959 is shown in figure 4. The November 1958 to June 1959 portion of the graph has been placed under the corresponding months of 1957 and 1958 to simplify a comparison of similar seasons. It can be seen that the seasonal occurrence has not been altered by the immersed ore. The January 1959 to April 1959 zero count cannot be considered significant as far as the copper ore experiment is concerned because of the subsequent rise that followed the pattern of the previous year.

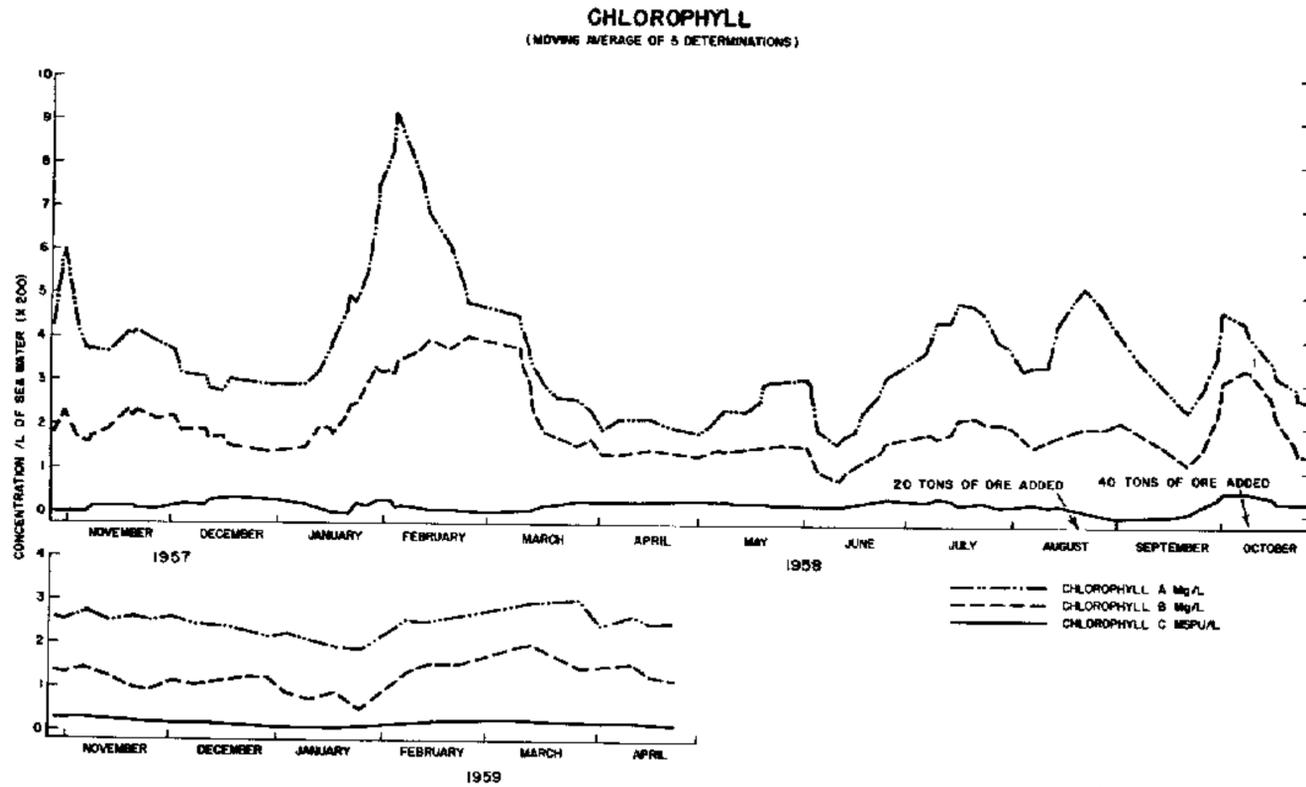


FIGURE 2.—Average chlorophyll concentration of East Lagoon from station samples.

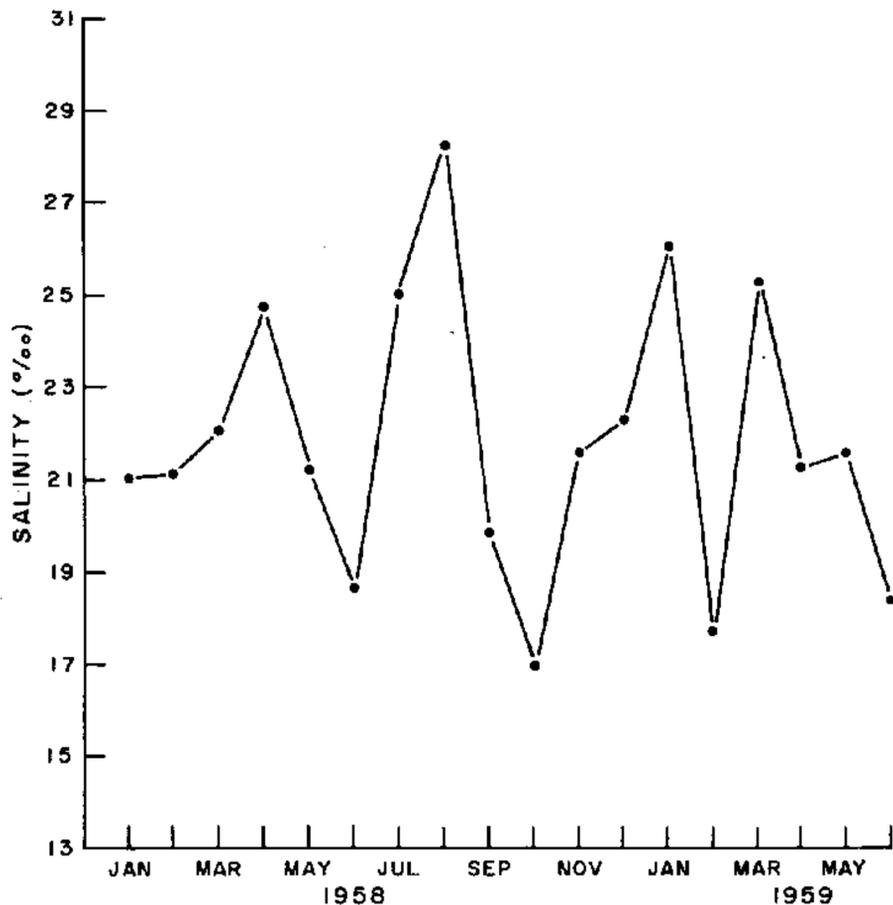


FIGURE 3.—Salinity of East Lagoon showing monthly averages.

**Copper**

Twenty tons of ore were added to the lagoon August 21, 1958. The effect of this addition on the overall copper concentration based on the average of station results is shown in figure 5. A maximum of 0.14  $\mu\text{g. at. Cu/l.}$  was attained in less than a week but was reduced to the low value shown by the excessive tidal and drainage dilution that accompanied hurricane "Ella". The low

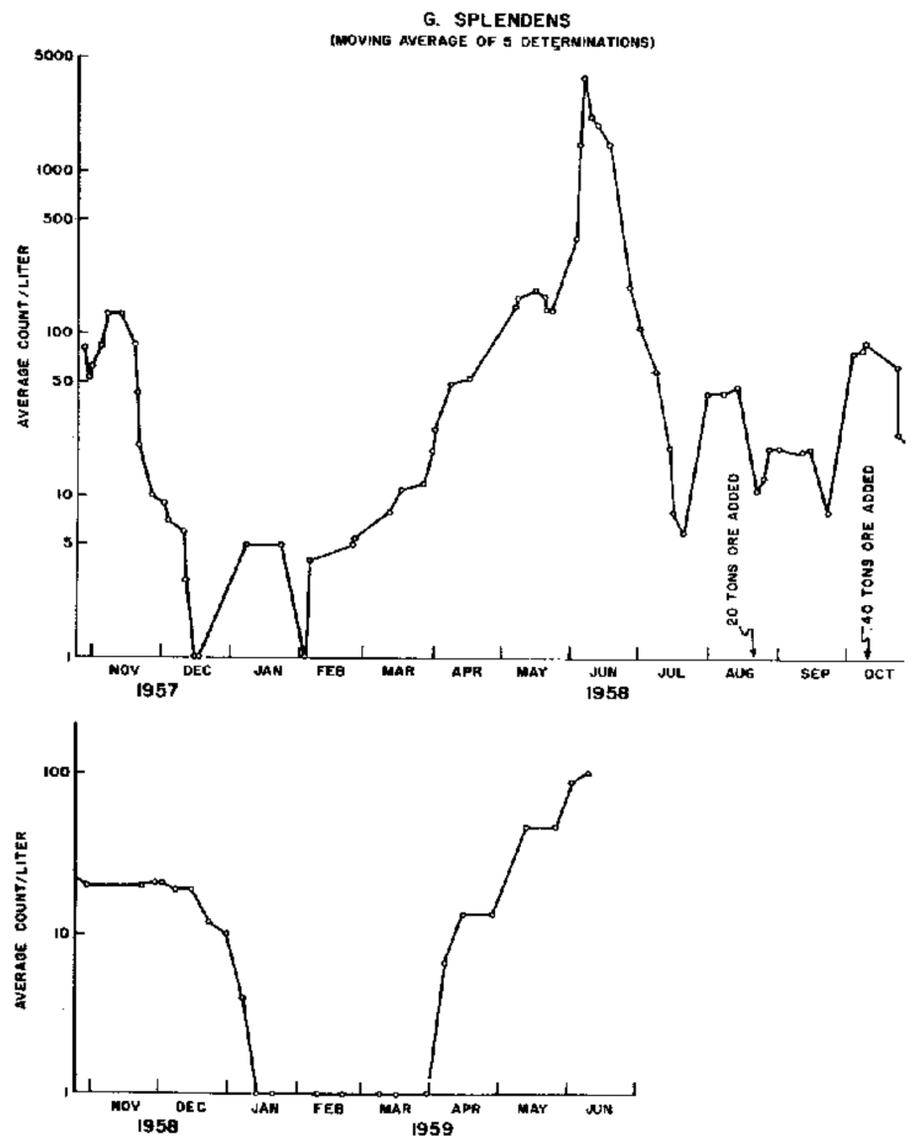


FIGURE 4.—*Gymnodinium splendens* (average counts for all stations).

maximum of 0.14  $\mu\text{g. at. /l.}$  indicated that a second and larger addition would be necessary to obtain a copper concentration lethal to *G. breve*. Accordingly, on October 21 an additional 40 tons were

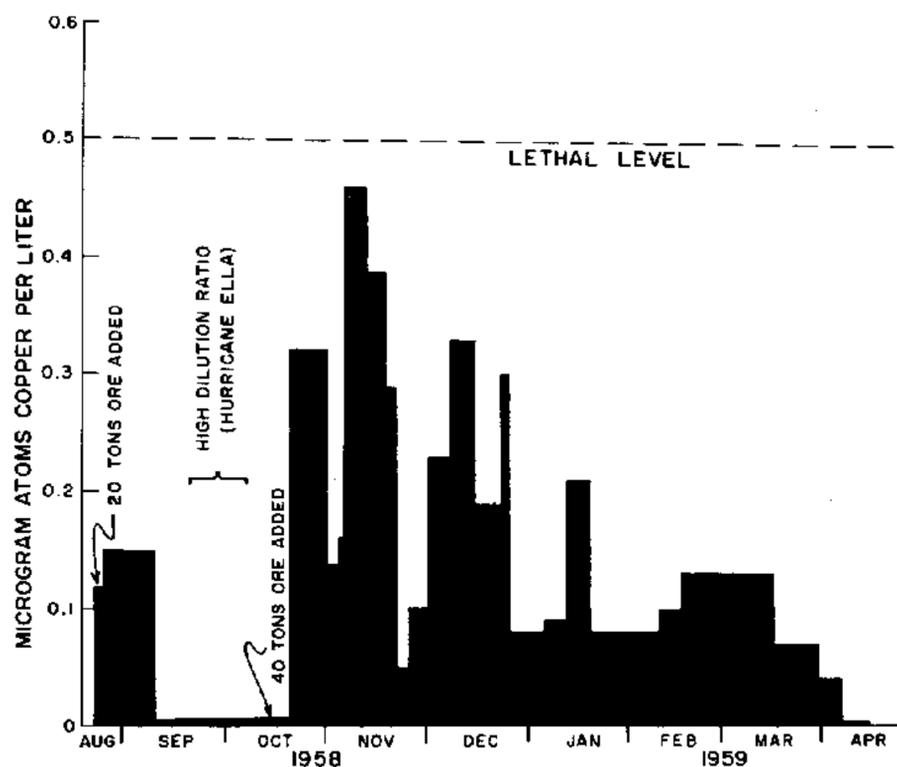


FIGURE 5.—Copper concentrations (average of all stations) showing approximate minimum lethal level from laboratory experiments.

placed in the lagoon. Again the results were disappointing. A near lethal concentration was attained but decreased during the next 5 months to about  $0.01 \mu\text{g.at./l.}$  In some respects, the effects of the ore were similar to those of copper sulphate employed in the Florida red-tide control experiments (Rounsefell and Evans, 1958). The rapidly attained maximum levels soon decreased to normal values for the area. In the Florida control tests, however, lethal levels were reached, and the decline that followed occurred in a matter of days rather than months. Undoubtedly, variation in the hydrography and chemistry of the two areas accounted for much of the difference in maximum levels attained and also in the rates of decline. The water of the lagoon is high in particulate matter (fig. 6), and the copper from the ore was assumed to have been adsorbed and made unavailable by the muds, plankton organisms, and other

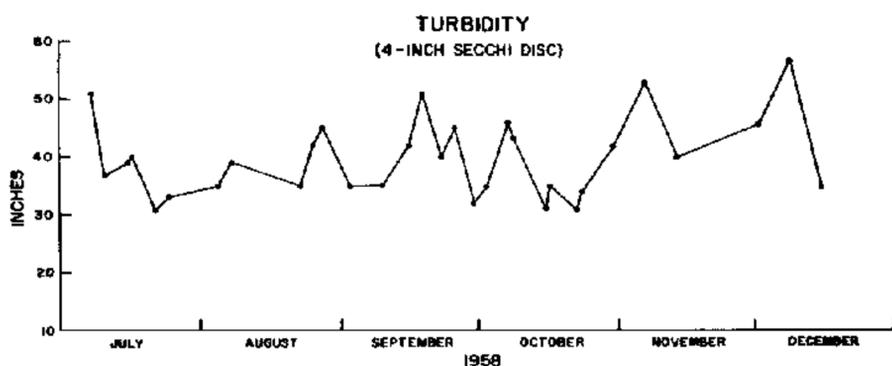


FIGURE 6.—Turbidity of East Lagoon. Average Secchi disk readings from stations.

material making up the particulate matter (Harvey, 1955).

#### Zooplankton

A qualitative and quantitative study of the standing crop of zooplankton in the lagoon was made by Fleminger (1959). The outstanding observation of his work was the broad summer-abundance peak and secondary peak combined with troughs in the early spring and autumn (fig. 7). Of particular significance is the January to March 1959 secondary peak which indicates continued growth of zooplankton populations following the addition of copper ore.

#### Barnacle setting rate

This study, conducted by Aldrich (1958a), showed that the adult barnacle population of the lagoon consisted almost exclusively of the brackish-water species, *Balanus eburneus*. Another brackish-water species found occasionally was *Balanus improvisus*. The data in figure 8 indicate the seasonal nature of barnacle setting in the lagoon. The outstanding feature is the continuance of the seasonal growth pattern after addition of the ore.

#### *Prorocentrum* sp.

Table 1 shows the initial and final counts of *Prorocentrum* sp., and copper concentration of the cultures in the dialysis bags used in the lagoon. More than half of these cultures increased in population count. The data indicate that the greatest increase occurred in cultures having the lowest initial count. Presumably, these had not reached their peak when placed in the lagoon.

The copper concentration apparently did not interfere with the population growth of the organism. There was one exception: approximately 60 percent mortality occurred within the 4-day bags placed at station 4 on October 10. This was the day of the second ore addition (table 1), and the day that the greatest concentration of copper was observed within the bags.

#### Live car organisms

Laboratory experiments (Aldrich, 1958b) conducted in conjunction with the copper ore study indicated that the snail *Littorina irrorata* was probably most susceptible to copper poisoning. Twenty-four-hour tests demonstrated, however,

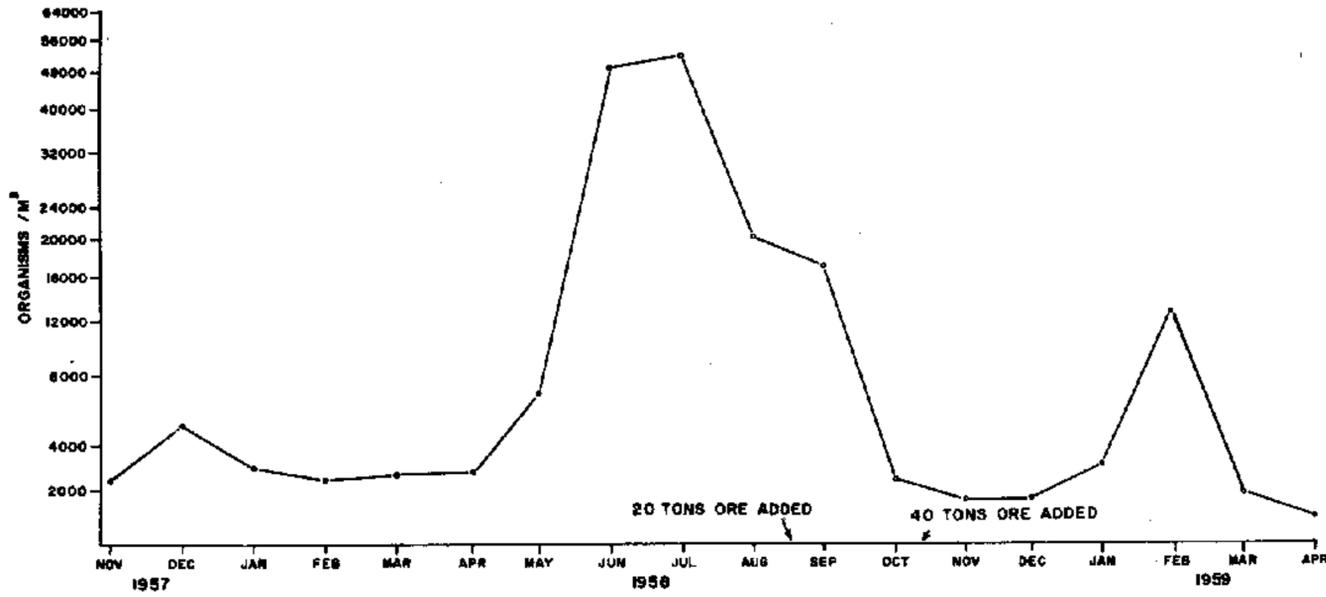


FIGURE 7.—Zooplankton concentration. Average of plankton samples taken at stations 1, 3, and 7.

TABLE 1.—Summary of dialysis bag data showing initial and final counts of organisms and final copper content of bags placed in East Lagoon, after addition of ore

Date	Days in lagoon	Count/.01 ml.		Copper $\mu\text{g. at./l.}$
		Initial	Final	
Aug. 23	4	43	43	0.19
25	2	21	50	.17
25	4	21	48	.18
27	2	52	39	.28
27	4	52	41	.24
29	2	48	42	.26
29	4	48	42	.21
Oct. 10	2	32	42	
10	4	32	40	.41
12	2	35	36	.32
12	4	35	39	
14	2	12	37	.12
14	4	12	26	.13
16	2	24	24	.25
16	4	24	26	.19
18	2	22	16	.20
18	4	22	25	.18

<sup>1</sup> About 60 percent of the organisms in the bags at Station 4 were dead.

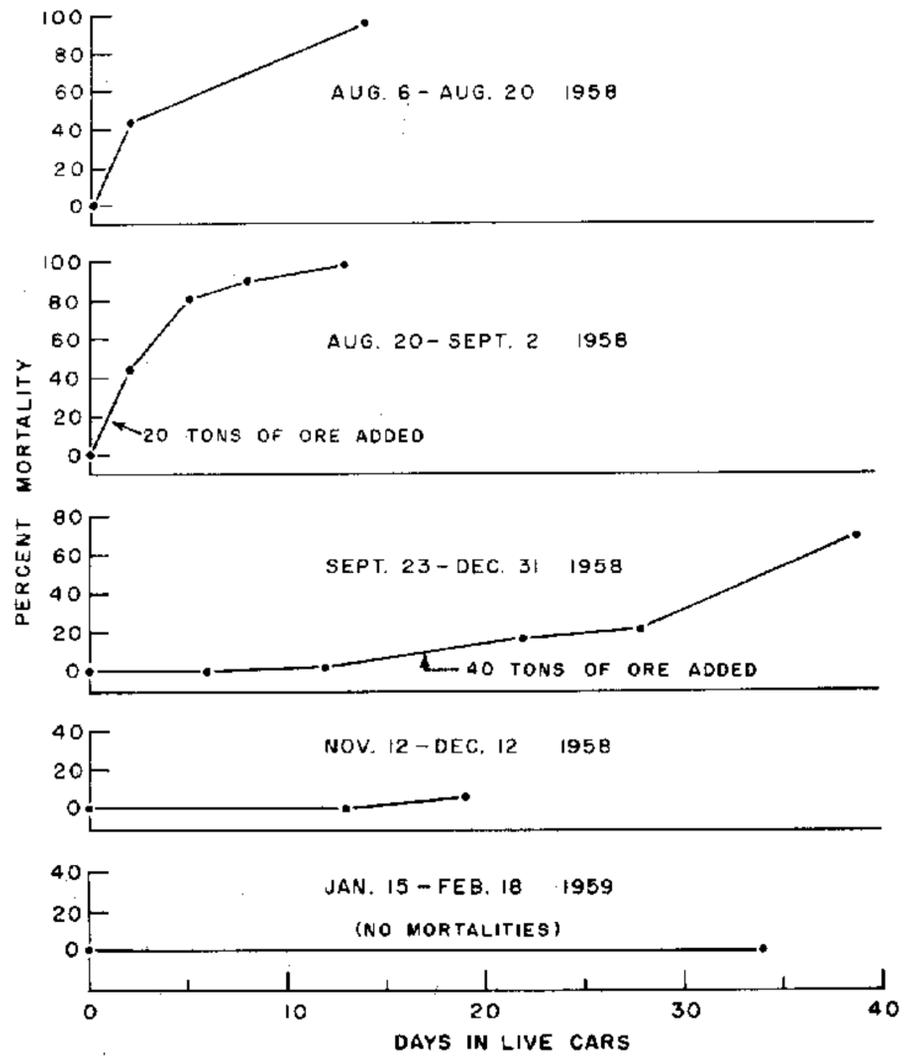


FIGURE 9.—Mortality of *Littorina irrorata* in East Lagoon.

that the snail could tolerate copper concentrations of 8  $\mu\text{g. at./l.}$  with only temporary minor discomfort. The mortality rate of this organism for five test periods is shown in figure 9. The snails represented by the August 6 to September 2 periods were a generation older than those used in subsequent experiments. We believe increased age was the cause of greater mortality rate shown. The decrease in mortality following the addition of the copper ore indicates that the ore had little or no detrimental effect on this organism. The relatively small increase of the copper concentration

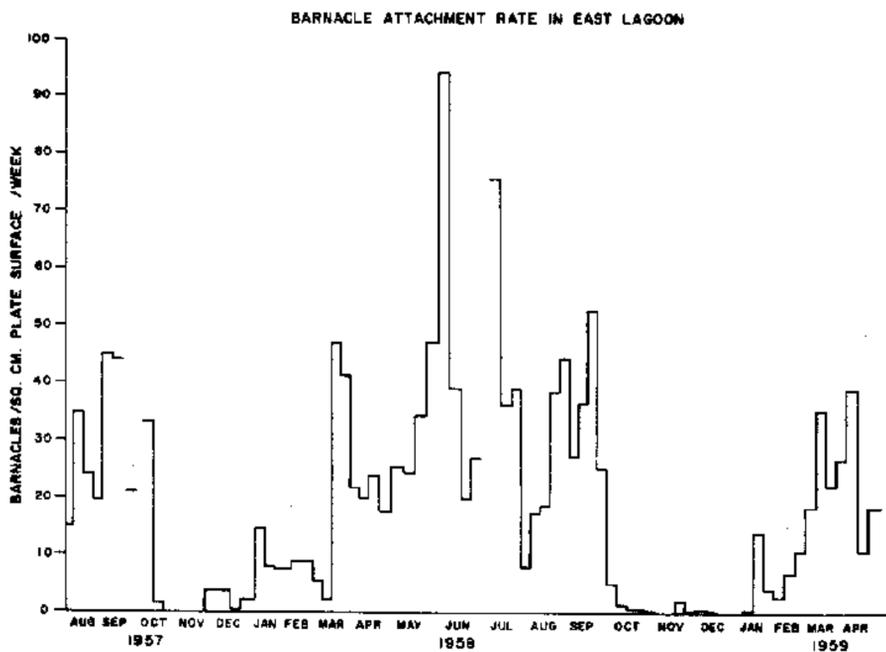


FIGURE 8.—Barnacle attachment in East Lagoon.

in the lagoon apparently did not have a significant effect on the mortality rates of the other species in the live car.

### DISCUSSION

Experiments conducted in our laboratories indicate that more copper ore is required to reach the toxic level for *Gymnodinium breve* in lagoon water than in Florida coastal water. This is thought to be due to the large amounts of natural chelators and particulate matter present in the lagoon as opposed to the relatively clear Florida waters. On the other hand, the Florida coastal waters receive more tidal flushing and dilution than the lagoon, and we would expect the maximum level of copper concentration to be less permanent than that shown for the lagoon in figure 5. Even assuming a toxic level could be reached in the Florida coastal waters, large quantities of ore would have to be added at frequent intervals which would make the cost prohibitive.

### SUMMARY

An analysis of the biological and chemical data shows that the copper concentration of the lagoon was not increased to a level lethal to *Gymnodinium breve* after the addition of 60 tons of ore. The flora and fauna of the lagoon and organisms placed there in dialysis bags and live cars showed no significant effect attributable to the ore. The copper level, after the addition of the ore, increased to a maximum that was below the laboratory estimate of the level toxic to *G. breve* (based on Florida sea water) and then dropped to a lower level. These results show that the ore is not capable of maintaining a sufficiently high copper concentration to be considered as a means of controlling red tide outbreaks in waters similar in quality to that of the lagoon.

Results of this experiment indicate that copper ore does not have the desired characteristics of a red tide controlling agent, and we recommend that it not be used.

### LITERATURE CITED

- ALDRICH, DAVID V.  
1958a. Barnacle attachment rates at Galveston, Texas. U.S. Department of the Interior, Fish and Wildlife Service, Annual Report of the Gulf Fishery Investigations for the year ending June 30, 1958, p. 89.
- 1958b. Toxicity of copper to marine organisms. U.S. Department of the Interior, Fish and Wildlife Service, Annual Report of the Gulf Fishery Investigations for the year ending June 30, 1958, p. 86.
- CHOW, TSAI HWA J., and THOMAS G. THOMPSON.  
1952. The determination and distribution of copper in sea water. *Journal of Marine Research*, vol. 11, No. 2, pp. 124-138.
- CREITZ, GRACE I., and FRANCIS A. RICHARDS.  
1955. The estimation and characterization of plankton populations by pigment analysis. III. A note on the use of "Millipore" membrane filters in the estimation of plankton pigments. *Journal of Marine Research*, vol. 14, No. 3, pp. 211-216.
- DAVIS, CHARLES C.  
1948. *Gymnodinium brevis* sp. nov. a cause of discolored water and animal mortality in the Gulf of Mexico. *Botanical Gazette*, vol. 109, No. 3, pp. 358-360.
- FEINSTEIN, ANITA, A. RUSSELL CEURVELS, ROBERT F. HUTTON, and EDWARD SNOEK.  
1955. Red tide outbreaks off the Florida west coast. Marine Laboratory, University of Miami, Report 55-15 to the Florida State Board of Conservation, 44 pp.
- FLEMINGER, ABRAHAM.  
1959. East Lagoon zooplankton. In Galveston Biological Laboratory fishery research for the year ending June 30, 1959. Bureau of Commercial Fisheries, U.S. Fish and Wildlife Service, Circular 62, pp. 114-118.
- GATES, JEAN A., and WILLIAM B. WILSON.  
1960. The toxicity of *Gonyaulax monilata* Howell to *Mugil cephalus*. *Limnology and Oceanography*, vol. 5, No. 2, pp. 171-174.
- GUNTER, GORDON.  
1942. Recurrent summer fish mortalities on the Texas coast. *American Midland Naturalist*, vol. 28, p. 631.
- HARVEY, H. W.  
1955. The chemistry and fertility of sea water. Cambridge, England, University Press, 224 pp.
- HOSTE, J., J. EECKHOUT, and J. GILLIS.  
1953. Spectrophotometric determination of copper with cuproine. *Analytica Chimica Acta*, vol. 9, pp. 263-274.
- RICHARDS, FRANCIS A., with THOMAS G. THOMPSON.  
1952. The estimation and characterization of plankton populations by pigment analyses. II. A spectrophotometric method for the estimation of plankton pigments. *Journal of Marine Research*, vol. 11, No. 2, pp. 156-172.
- ROUNSEFELL, GEORGE A., and JOHN E. EVANS.  
1958. Large-scale experimental test of copper sulphate as a control for the Florida red tide. U.S. Department of the Interior, Fish and Wildlife Service, Special Scientific Report—Fisheries No. 270, 57 pp.

WILSON, WILLIAM B.

1959. Evaluating toxicity of dissolved substances to microorganisms using dialysis membranes. In Galveston Biological Laboratory fishery research for the year ending June 30, 1959. Bureau of Commercial Fisheries, U.S. Fish and Wildlife Service, Circular 62, pp. 100-102.

ZEIN-ELDIN, ZOULA P.

1959. Plankton pigments in East Lagoon. In Galveston Biological Laboratory fishery research for the year ending June 30, 1959. Bureau of Commercial Fisheries, U.S. Fish and Wildlife Service, Circular 62, pp. 106-107.